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# Bioelectrochemical Systems for Energy Valorization of Waste Streams

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## Abstract

Bioelectrochemical systems (BES) encompass a group of technologies derived from conventional electrochemical systems in which the electrodic reactions are directly or indirectly linked to the metabolic activity of certain types of microorganisms. Although BES have not yet made the leap to the commercial scale, these technologies hold a great potential, as they allow to valorize different liquid and gas waste streams. This chapter is devoted to exploring some of the possibilities that BES offer in the management and valorization of wastes. More specifically, it focuses on analyzing practical aspects of using BES for energy valorization of wastewaters and CO<sub>2</sub>-rich streams. Here, it is shown how BES can compete, in terms of energy usage, with conventional wastewater treatment technologies by exploiting the energy content of some of the chemicals present in the wastewater. Moreover, it explores how BES could enable using wastewater treatment plants as load regulation system for electrical grids. It also includes some insights on the capability of BES to recover valuable products such as fertilizers from wastes, a feature that allows this technology to promote energy efficiency in the fertilizers industry, and a sector that demands substantial amounts of energy in our world today. Finally, some of the most relevant scale-up experiences in the field are also covered.

**Keywords:** bioelectrochemical systems (BES), wastes valorization, wastewater, CO<sub>2</sub>, nutrients recovery, energy efficiency

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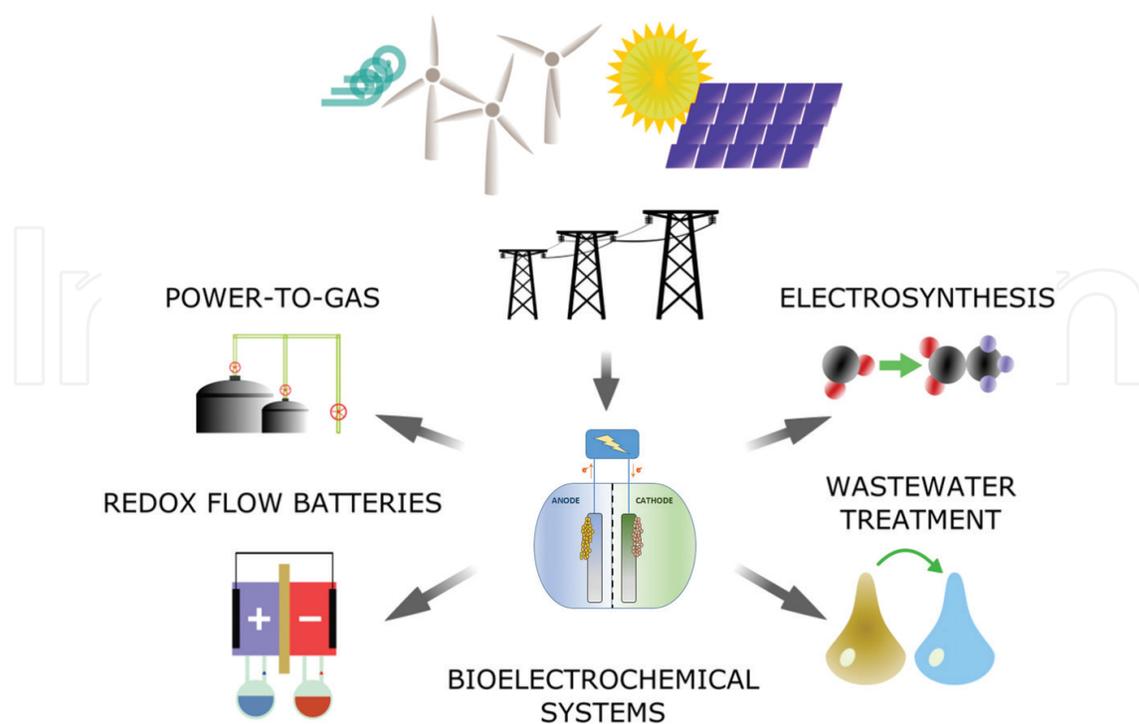
## 1. Introduction

From a practical point of view, it can be said that bioelectrochemical systems (BES) are conventional electrochemical systems that convert chemical energy into electrical energy (and

vice versa) using microbes as catalysts [1]. Although the ability of certain bacteria to generate electrical current was first described more than 100 years ago [2], it was not until the beginning of the present century that this phenomenon started to draw real interest from scientists and engineers. During the last 15 years, the progress made in the fields of bioelectrochemistry and BES has allowed to take the leap from the laboratory to the pilot scale [3, 4] so that commercial development seems to be at hand.

Initial research efforts were focused on exploring the possibilities that BES offered for the treatment and energy valorization (as electric power or hydrogen) of diverse waste streams [5, 6]. To date, the range of applications has broadened dramatically, extending to diverse fields such as desalination [7], bioremediation of contaminated water and soils [8], nutrients recovery [9], or the synthesis of valuable chemicals [10], among many others. Moreover, the versatility and multifaceted nature of BES open the way for applications that lay far beyond bio-based industrial processes. Indeed, when BES are operated in electrolytic mode (see Section 2 in the present chapter), they demand a certain amount of electrical energy, part of which ends up stored in chemical products (hydrogen, methane, etc.). This feature opens the way to using BES as an alternative technology for storing excess electrical power within electrical grids [11]. Thus, BES would offer new storage opportunities, especially in decentralized smart grids, providing a nexus with the waste management systems and offering alternative waste and energy management strategies.

This chapter explores some of the most relevant opportunities that BES offer for energy valorization of waste streams (**Figure 1**). It begins by briefly describing the principles of operation

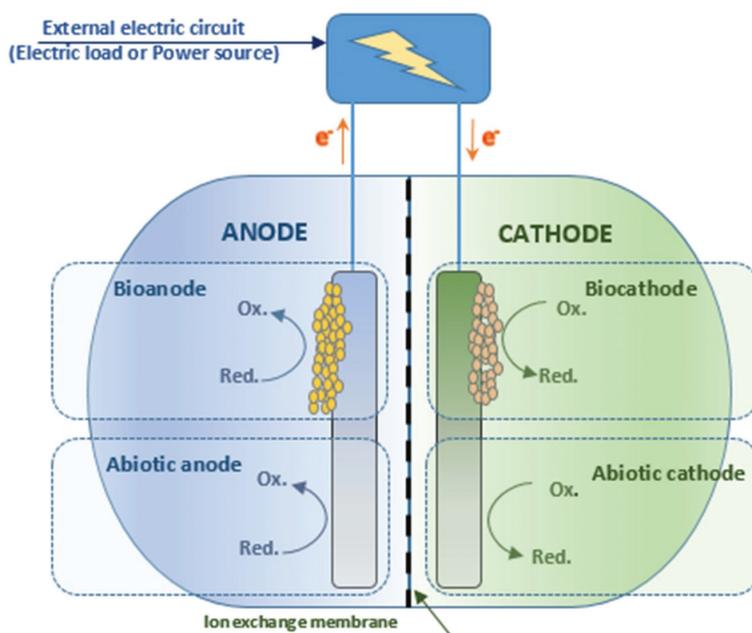


**Figure 1.** Scope of applications of BES for energy valorization of wastes.

of BES and how they can become useful in energy valorization of wastewaters. It also covers the valorization of CO<sub>2</sub>-rich streams paying special attention to fuels production. BES can also bring significant energy savings for the fertilizers' production industries. Given the large amounts of energy that fertilizers producing industries demand around the globe [12, 13], another subsection is devoted to the use of BES for nutrients recovery from wastes. The chapter ends by reviewing the latest pilot scale experiences.

## 2. Bioelectrochemical systems: What they are?

BES can be understood as electrochemical systems in which at least one of the electrode reactions (anodic and/or cathodic) is biologically catalyzed [14]. They share with traditional electrochemical systems the key feature of being operationally reversible, i.e., they can be run as galvanic cells (the redox reactions are spontaneous) or as electrolytic cells (the redox reactions are non-spontaneous and require a certain amount of electrical energy to proceed). The first BES prototypes operated in galvanic mode were termed as microbial fuel cells (MFC), and when they were operated in electrolytic mode, they were usually referred to as microbial electrolysis cells (MEC). Although this terminology has been somehow transcended as a result the increasing number of BES typologies and architectures that have appeared during the past decade [15], it remains still useful as it mirrors the two basic modes of operation in electrochemical systems. **Figure 2** shows a schematic representation of the principle of operation of BES systems. For more detailed information about the basic principles of BES, the reader is referred to [15].



**Figure 2.** Schematic representation of the principle of operation of a BES. "Ox." stands for oxidized compound, while "red." stands for reduced compound.

### 3. BES for wastewater valorization

#### 3.1. BES for wastewater treatment and power production

First published studies on MFC and MEC technologies were mainly devoted to further the understanding of how operational parameters (pH, temperature, etc.) affect their performance and to the development of new reactor configurations and new strategies to optimize their figures of merit. Most of these studies were carried out using synthetic media as electrolytes to allow researchers to keep control over substrate composition. Subsequent laboratory tests with real wastewaters served to gain knowledge of the real world potential of MEC and MFC. These studies helped to quantify to which extent reactors performance gets affected by the presence of a real substrate. For instance, MFC fed with actual wastewater produced power densities (normalized to the surface area of the electrodes) in the range of several tens of  $\text{mW}\cdot\text{m}^{-2}$  (milliwatts per square meter of electrode) [16], which contrast with the hundreds [17] and even thousands of  $\text{mW}\cdot\text{m}^{-2}$  [18] achievable with synthetic effluents. Despite recent advances in electrode materials and reactor configurations [19], power production in MFC has not improved significantly. Issues such as low conductivity and low buffer capacity are often cited as the main factors that explain the observed poor performances [20]. Unquestionably, MEC has to face similar challenges, although economic feasibility criteria seem to be less stringent [21]. For instance, it has been estimated that the target total internal resistance for MEC technology to be cost effective is  $80 \text{ m}\Omega\cdot\text{m}^{-2}$ , while for MFC this target becomes much more restrictive ( $40 \text{ m}\Omega\cdot\text{m}^{-2}$ ) [21]. Moreover, the difference in architecture between a microbial MFC and MEC poses further problems with scaling up. With a pilot scale MFC, aeration to the cathode invites complex issues, as either the cathode cell must be open to the air or there is an added cost of aeration. However with an MEC, the cathode is anaerobic, making the design of a larger system simpler, all of which outlines a more favorable scenario for MEC.

#### 3.2. BES for wastewater treatment and chemical energy storage

Due to its ubiquitousness and the enormous volumes produced globally each year [22], urban wastewater is perhaps the most straightforward waste stream for MECs. The first MEC operated on urban waste water (batch with retention times between 30 and 108 h) offered quite promising results in terms of organic contamination removal (almost 100% removal efficiency), although hydrogen recovery was relatively low (~10% of the theoretical maximum) [23]. In a later study, using urban wastewater as fed as well, it was possible to produce hydrogen at a rate of  $0.3 \text{ L}_{\text{H}_2}\cdot\text{L}_{\text{R}}^{-1}\cdot\text{d}^{-1}$  (liter of hydrogen per liter of reactor per day) in a 100 mL (total volume) continuously operated MEC (hydraulic retention times between 3 and 24 h) [24], and energy consumption figures ( $\sim 1.5 \text{ Wh}\cdot\text{g}\cdot\text{COD}^{-1}$  (watts-hour per gram of chemical oxygen demand removal)) were similar to those typically found for conventional wastewater technologies [25]. However, when this same MEC design was replicated to a larger scale (3.3 L), hydrogen production declined significantly ( $0.01 \text{ L}_{\text{H}_2}\cdot\text{L}_{\text{R}}^{-1}\cdot\text{d}^{-1}$ ) and energy consumption rocketed. In a more recent study performed at a higher scale (130 L) it has been reported energy recoveries of up to 121% with respect to the electrical input [3]. Despite the still important challenges that MECs need to overcome [11], these figures highlight the potential of this technology for exploiting the often untapped energy

content of WW [26]. This manifests more clearly if we bring to mind that conventional wastewater treatment plants do not only make use of this potential but also demand large amounts of energy. For example, in Spain, wastewater treatment accounts for approximately 1% of the total energy consumed [27]. BES would enable using the wastewater treatment plants not only as facilities for water contamination removal but also as an electrical regulation system, stocking the surplus of energy in the grid as hydrogen or methane [28]. In this sense, redox flow batteries (RFB), which may become a strategic partner in MEC implantation [29], could offer new possibilities to enhance energy management capabilities of MEC. RFB are electrochemical energy storage devices with a quite interesting feature: they allow to decouple power from energy output [30]. Thus, the reducing power obtained in MEC reactors treating waste streams could be stored in an electrolyte solution that would be easily used for electricity generation or in a subsequent electrochemical process. Well-known RFB, such vanadium systems, presents serious environmental pitfalls for its use in massive energy storage applications [31], but recent approaches, like all-organic RFB [32], could open a wider field. Here, the main candidates are quinone-based molecules [33], which, interestingly, have been previously studied in BES as they may act as intermediates in electron transfer mechanisms [34].

Together with urban wastewater treatment facilities, industrial environments represent another clear niche for potential application of MECs. In general, hydrogen production and energy consumption in MEC improve as the organic concentration in the WW increases. In this sense, industrial wastewater, which usually contains high organics concentration, is an ideal waste effluent for MEC. For instance, by feeding a MEC with the effluent of an ethanol-producing reactor, Lue et al. [35] achieved an impressive hydrogen production rate of  $\sim 2 \text{ L}_{\text{H}_2} \cdot \text{L}^{-1}_{\text{R}} \cdot \text{d}^{-1}$  with an electrical energy efficiency of 287%. Still, the use of industrial effluents in MEC may present significant shortcomings. On the one hand, sometimes their composition is not well balanced and may require some nutrient amendment [36], which may not always result in an economically or environmentally feasible approach. On the other hand, dealing with high organic contraction, wastewater in MEC may become an important challenge as it may favor the proliferation of undesired microorganism that could hinder the activity of the electrogenic microorganisms [11].

#### 4. BES for CO<sub>2</sub> valorization

Increasing atmospheric CO<sub>2</sub> concentration is widely seen as the main driving factor behind climate change [37]. CO<sub>2</sub> capture at large emission sources (such as power plants) and subsequent sequestration (mainly in geological or deep sea storage sites) has been put forward as a suitable strategy to limit CO<sub>2</sub> accumulation in the atmosphere [38], although this approach arouses significant public concern [39]. Another alternative more favorable to public opinion and that may help to offset the cost of reducing CO<sub>2</sub> emissions is the use of this gas as a feedstock for industrial processes. In this regard, one among many possibilities is the conversion of CO<sub>2</sub> into valuable chemicals or fuels. The main issue here is that CO<sub>2</sub> is the least energetic (most oxidized) form of carbon, and thus, a substantial amount of energy is required to convert it into useful reduced chemicals. For instance, the Sabatier process that converts CO<sub>2</sub>

and  $H_2$  into  $CH_4$  requires high temperature and pressure [40], which usually implies significant energy requirements. Here, BES can provide a suitable alternative through a bioprocess known as microbial electrosynthesis (MES), which requires much milder conditions. MES is a proof-of-concept technology that converts  $CO_2$  into valuable chemicals and fuels within a BES. MES meets the requirements of green chemical technologies as it uses microorganisms as inexpensive and sustainable catalysts, can be operated at ambient conditions, and can be fed with contaminants ( $CO_2$ ) for environmental remediation [41]. Later, we review some of the target products that can be obtained through MES, paying special attention to alcohols and methane, as these molecules can be easily used as energy carriers in many applications.

*Volatile fatty acids (VFA).* VFA are the most studied group of chemicals synthesized in MES. These slightly reduced organic compounds can be produced from  $CO_2$  by a wide variety of microorganisms following different metabolic pathways. Homoacetogens in particular are responsible for acetate production, and recent studies have reported acetic acid production rates above  $0.78 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ , product titers of up to  $13.5 \text{ g}\cdot\text{L}^{-1}$ , and current-to-acetate conversion efficiencies of 99% [42, 43]. Butyric acid is the second most reported VFA on MES systems. This C4 VFA has mainly been observed as a co-product in acetic acid production systems, although some studies also target this product as main objective [44]. Among the later, production rates of up to  $0.16 \text{ g}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$  and maximum titers of  $5.5 \text{ g}\cdot\text{L}^{-1}$  at relatively low conversion efficiencies (40%) have been achieved [45]. Other VFAs such as propionic, isobutyric, or medium chain fatty acids have been found as by-products in lower concentrations in acetic/butyric acid-producing MES systems showing low energy efficiency so far [44].

*Alcohols.* Bioethanol is a renewable fuel subjected to strong controversy as its production is related to deforestation and to the rising of food prices. MES offers the opportunity of obtaining ethanol from  $CO_2$ -rich streams thus avoiding any concern derived from land-use changes. Although ethanol can be produced directly from  $CO_2$ , its production from acetate is thermodynamically and energetically more favorable, providing that the undissociated acid exists in a slightly acidic medium [46]. Still, ethanol production through MES is far from becoming a feasible process yet as titers and efficiencies are relatively low (up to  $0.5 \text{ g}\cdot\text{L}^{-1}$  and 55%, respectively) [46]. Butanol can also be produced in MES following a similar pattern as in ethanol (butanol begins to appear in butyric acid-producing MES when sufficient reducing agents are present). Butanol has been found as a by-product but not targeted as main product until date, and therefore, the low rates and efficiencies are not representative of its real future potential yet [44]. Other alcohols have been obtained through MES. Arends et al. [47] firstly produced isopropanol in a  $CO_2$ -fed continuous MES system, achieving titers up to  $0.82 \text{ g}\cdot\text{L}^{-1}$ . Soussan et al. [48] reported the possibility of producing glycerol when succinate was present together with  $CO_2$  in the feed. About 100%  $CO_2$ -glycerol selectivity was achieved with titers from 6.0 to 9.0 mM.

*Methane. Bioelectrochemical power-to-gas.* Methane is a valuable energy carrier and a fuel with low environmental impact compared to other fossil fuels. It can be produced from  $CO_2$  through MES by taking advantage of the ability of some microorganisms (e.g., methanogenic archaea) of using a solid surface (cathode) as electron donor. First published experiences reported production rates of  $4.5 \text{ L}_{CH_4}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$  and efficiencies up to 80% [49]. More recent studies have succeeded in improving the overall efficiency reaching maximum production

rates of  $30.3 \text{ L}_{\text{CH}_4} \cdot \text{d}^{-1} \cdot \text{m}^{-2}$  and efficiencies near 100% [50], yielding high grade gas streams with methane content over 95%, thus opening the opportunity for injection in the natural gas grids.

Another interesting application of these bioelectromethanogenic systems is biogas upgrading. The biogas produced during anaerobic digestion of wastes usually contains large amounts of  $\text{CO}_2$  (typically 30–40%), and so to improve its energy value some kind of refinement is usually required [51]. MES can become an alternative to membrane, absorption, or scrubbing units to remove  $\text{CO}_2$  from the biogas with the advantage of converting it into more methane. Current studies on using MES for biogas upgrading have been able to keep  $\text{CO}_2$  content in the off-biogas permanently below 10%, showing efficiencies over 80% [51, 52]. Although anaerobic digestion and BES have been traditionally seen as two bio-based technologies competing for the same application niches, here we see that both AD and BES can be integrated to overcome some of their inherent limitations.

These studies are revealing that microbial catalyzed reactors are capable of producing a wide spectrum of chemical building blocks, leading to the basis of a renewable chemical platform which might be the future substitute of petroleum-based chemistry. The interaction between distributed electricity grids into delocalized chemical production facilities is extremely attractive, giving a new extension to the biorefineries concept.

## 5. BES for nutrients recovery from waste streams

Plant macronutrients—mainly nitrogen, phosphorus, and potassium—are indispensable elements for the growth of every living beings. However, when supplied to the soil as chemical fertilizers, they can bring about serious environmental issues (e.g., eutrophication of water bodies and greenhouse gases emissions). World population growth and the ever-increasing demand for agricultural products urge the need for an adequate use of fertilizers to avoid not only their undesired environmental impact but also an eventual depletion of the limited mineral deposits, especially phosphate rock [53]. Furthermore, fertilizers production consumes significant amounts of energy, which brings additional environmental and economic concerns. For instance, 3% of total natural gas production in United States is diverted to the fertilizers industry [12], and fertilizers application in China absorbs 4.4% of China's total primary energy use [13].

Nutrients recovery from wastes can prove to be a feasible strategy to tackle both environmental and energy issues simultaneously. On the one hand, it allows to limit the amount of nitrogen and phosphorus discharged into the environment, and on the other hand, it may help to reduce the energy intensity in fertilizers production. There are several technologies available for nutrients recovery from organic wastes, among which struvite precipitation occupies a preeminent position [54]. BES can also offer the possibility of recovering nutrients from waste streams, and thanks to their ability for harnessing the bioenergy present in the organic matter, they also help to offset the energy usage [55]. Most of the research studies in the literature are mainly focused on the use of nitrogen and phosphorus recovery [56], as these two nutrients are usually found in many organic wastes.

For nitrogen in particular, this element can be concentrated (usually as ammonium) on the catholyte of the BES by migration and diffusion from the anode side. Due to the high pH of the catholyte, ammonium turns into ammonia gas which can be subsequently stripped from the off-gas [57]. The use of BES for nitrogen recovery has been explored using different waste streams, such as swine wastewater, landfill leachate or urine, and different reactor configurations offering encouraging results [58, 59]. Zamora et al. [60] demonstrated that electrical energy required in a pilot scale BES for ammonia recovery is  $1.4 \text{ kWh}\cdot\text{kg}_N^{-1}$ , which is lower than other electrochemical nitrogen recovery technologies (for instance,  $13 \text{ kWh}\cdot\text{kg}_N^{-1}$  is needed to recover nitrogen for digestate using a conventional electrochemical cell [61]). Moreover, some studies have even reported a positive energy balance producing a surplus of  $0.96 \text{ kWh}\cdot\text{kg}_N^{-1}$  [62].

BES also represents an ideal technology to precipitate phosphorus, together with ammonium, in the form of struvite thanks to the relatively high pH in the catholyte as mentioned before. Furthermore, BES can be used to mobilize orthophosphate from the iron phosphate contained in digested sewage sludge [63]. Cusick et al. [64] reported a P precipitation efficiency of 85% with an associated energy consumption of  $6.5 \text{ kWh}\cdot\text{kg}_P^{-1}$ , which was significantly less than that needed by other struvite formation methods based on pH adjustment.

Therefore, the main advantage of using BES for nutrients recovery, compared to other technologies, is that they allow to limit the energy requirements by exploiting the energy content of the organic matter present in a waste [55]. Finally, although the first experiences with pilot plants have already been carried out and give hope to the development of this technology, the use of BES for nutrients recovery still needs optimization of operational parameters [65].

## 6. Scaling-up BES for energy valorization of waste streams

### 6.1. The challenges of scaling-up BES

Making the leap from the controlled laboratory scale use of these technologies into pilot scale systems that will inform us of their suitability to real applications is one of the most challenging aspects of research in this area. These challenges are mostly scientific, logistical, and financial in nature; here, we briefly discuss them. When conducting a pilot scale study, even with the best intentions and meticulous planning, it is not always easy to carry out the investigation strictly following the tenants of the scientific method. The use of replicas is a vital way of achieving a scientific method, the resulting reproducibility and reliability of the data collected is standard practice with all laboratory experiments. However, it is rarely considered at pilot scale, where the logistics and expense of operating one reactor are high enough without considering two. Ultimately, therefore most pilot scale studies are not highly scientific, and the information and conclusions we can draw from them are not as strong as those achieved in laboratory-based studies. This is unfortunate, as these studies will actually guide us into the real applications of the technologies developed initially in the laboratory. Achieving the rigor of laboratory testing within a field, a pilot scale study will be essential to take this technology forward.

The logistical problems of setting up a pilot scale project may individually seem like minor and highly surmountable problems, but can combine to have significant detriment to both the financial cost of the project and its outcomes. These problems, and the compromises that need to be made to overcome them, can have significant and long-lasting impacts into the study being undertaken. For example, a reactor planned for startup in the summer months can be delayed into the winter months which in the United Kingdom is a significant decrease in operating temperature, and would result in very slow microbial growth, and potentially a less active and effective biofilm forming. Without a replica reactor started in the summer months, we are unlikely to know the full impact of this on overall reactor performance.

Financial problems can be broadly split into two main areas, finding funding to do this research and then using this funding to build practical systems. BES technologies and the complex microbiology they rely on mean that they do not fit easily into the standard technology readiness levels often used to identify different funding sources. Many of the fundamental elements of BES operate differently at different scales. There is therefore a need to do basic and fundamental science (TR level 1) such as sequencing and understanding microbial dynamics on reactors that are prototypes in an operational environment (TR level 7). Secondly, once funding is in place, different materials need to be sourced which are affordable to use at large scale but will still function in the BES. Thankfully low cost alternatives to most of the materials have now been found, with stainless steel replacing platinum cathodes [66] and cheap battery separators replacing ion exchange membranes [67]. In 2008, these two components were 85% of the costs [20]; however, in recent pilots, they account for less than 2% [67]. The carbon anode material at approximately 100 £·m<sup>-2</sup> is now the greatest material cost. Furthermore, developing cheaper alternatives to ancillary equipments such as sensors and potentiostats, which are often expensive and not designed to be robust enough for field applications is another challenge.

## 6.2. A brief summary of the pilot scale studies undertaken in the area of BES

The first large-scale experience with BES was an MFC build and operated by the Advanced Water Management Center at the University of Queensland [68]. The MFC consisted of 12 units with a total volume of approximately 1 m<sup>3</sup>. There is scant information about the performance of this plant, although it is known that power production was limited by the low conductivity of the wastewater and biomass proliferation on the cathode [69]. In a much recent work based on a 200 L modular MFC operated in field conditions in a municipal wastewater treatment plant, Ge and He [70] reported more than 75% COD removal rates, accompanied by a power production of 200 mW, which was enough to power part of the ancillary equipment required to operate the plant. Much more complex substrates than urban wastewater have also been used as a feedstock for pilot MFC. In [71], it is reported that a 115 L MFC was able to remove almost all of the biodegradable fraction from swine manure producing about 200–400 mW of power. Moreover, the plant, which consisted of six MFC units, also allowed to remove about 50% of the nitrogen initially present in the manure.

The first large-scale MEC had a working volume of 1000 L, was a continuous flow, and ran a hydraulic retention time (HRT) of 1 day [66]. The system ran for a period 100 days, heated to 31°C, with an average influent of 760 ± 50 mgCOD·L<sup>-1</sup> (soluble chemical oxygen demand)

winery wastewater, along with some acetate supplement. COD reduction averaged 62%; however, hydrogen production was limited as the gas content was 85% methane. The system utilized a single chamber design, which resulted in methanogenesis occurring at the cathode, consuming the hydrogen. Although single chamber designs had been very efficient at the laboratory scale, this study showed that this was not scalable.

Few years later, Heidrich et al. [67, 72] built and operated a continuous flow MEC, which had a volume of 120 L, a HRT of 1 day, and ran for a period of 12 months using raw domestic wastewater ( $125\text{--}4500\text{ mgCOD}\cdot\text{L}^{-1}$ ) taken directly from the grit channels during pre-treatment. This was in the North East of England and the system was not heated, leading to temperatures ranging from 1 to  $20^\circ\text{C}$ . A low COD removal of 30% was reported; however, almost pure hydrogen ( $100 \pm 6.4\%$ ) was produced at a rate of  $0.015\text{--}0.007\text{ L}_{\text{H}_2}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ , with a coulombic efficiency (CE) of 41–55%. The cassette design of the electrodes that was developed in this study has seen to be versatile and scalable with its application in other pilots. The study did not reach the required energy recovery to be energy neutral and did not treat the wastewater to EU standards. Inconsistent COD balance, along with a build-up of sludge within the reactor was the cause of the poor performance.

In Ref. [4], a similar cassette electrode design but at two different scales:  $0.6\text{ m}^2$  and  $1\text{ m}^2$  anodes. It ran using settled domestic wastewater ( $347\text{ mgCOD}\cdot\text{L}^{-1}$ ), at a real treatment site at ambient temperatures ( $8.6\text{--}15.6^\circ\text{C}$ ) for 217 days, with a HRT of 5 h. By decreasing the spacing of the cassettes and increasing the HRT from the Heidrich study, the COD removal was on average 63.5%, and the effluent reached European Urban Wastewater Treatment Directive discharge standards [73]. However, the MEC only produced  $0.004\text{ L}_{\text{H}_2}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$  with a maximum CE of 27.7%. The problems arose from hydrogen-consuming bacteria entering the cathode compartment and scavenging hydrogen and maintaining a sterile cathode compartment were shown to be vital for successful hydrogen recovery [3].

This MEC used the primary effluent from domestic wastewater, running a 130 L MEC for a period of 5 months, at a temperature range of  $18\text{--}22^\circ\text{C}$ . Again this research team used the cassette style electrodes as the base for their design, with a HRT of 2 days. Hydrogen was produced at a rate of  $0.032\text{ L}_{\text{H}_2}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ , which is the highest yet published with a purity of 95%, and consequently, high cathodic gas recovery of 82% and an energy recovery of 121% with respect to the electrical input were achieved. However, COD removal was low at around 25%. This study also treated two types of synthetic wastewater utilizing the same design and discovered that hydrogen production was in fact the highest with real wastewater out of the three carbon sources tested. Although this system is the most successful yet in terms of energy production, problems still occurred, mainly related to application of electric potential and material deterioration.

## 7. Conclusions

The term bioelectrochemical systems (BES) encompass a group of relatively novel technologies which hold a great potential for energy valorization of a wide variety of waste streams.

Perhaps the clearest niche of application of BES lays in the field of wastewater treatment where this technology could help to improve the energy efficiency of the process by converting the energy content of the organic matter present in the wastewater into either electrical energy or a fuel gas. In fact, most of the pilot scale experiences developed to date have been designed for these purposes. Moreover, operational versatility of BES might bring additional opportunities for wastewater valorization, as they also allow to recover valuable chemicals and nutrients such as ammonium or phosphorus. Here, it is important to highlight that BES can perform this at a reduced energy and economic costs compared to more conventional technologies used in fertilizers industries.

Gaseous CO<sub>2</sub>-rich waste streams represent another suitable raw material for BES. Here, BES might provide a means for converting CO<sub>2</sub> into valuable organic chemicals such as methane or short chain fatty acids. This can potentially provide a cost-effective and environmentally friendly method for limiting CO<sub>2</sub> emissions into the atmosphere.

In short, BES can be seen as a group of technologies capable of valorizing a wide range of liquid to gaseous waste streams. In most cases, the operation of BES requires large amounts of electrical energy, most of which ends up stored in chemical energy (methane, hydrogen, etc.) that can be readily converted back into electrical energy when required by using well-established technologies (fuel cells, cogeneration, etc.). This feature would enable BES to operate as electrical regulation system which would bring further commercial opportunities for these technologies.

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